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(54) Title of the Invention: Water-Soluble Polysaccharide Film

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## SPECIFICATION

Title of the invention: Water-Soluble Polysaccharide Film

### Claims

A water-soluble polysaccharide film, characterized by containing carrageenan and galactomannan at a weight ratio of 99:1 to 20:80.

### Detailed description of the invention

The present invention relates to a water-soluble polysaccharide, and in particular, relates to a film having carrageenan as a component.

In the past, water-soluble polysaccharides, particularly edible water-soluble polysaccharides, have appeared on the market in the form of powders or particulate

materials, or as aqueous solutions. On the other hand, with the increasing diversity in eating habits occurring in recent years, interest has intensified in regard to edible water-soluble polysaccharides that can be formed into films. An example of a water-soluble polysaccharide that can be cited is carrageenan. Carrageenan is a substance that is extracted from seaweed of the Eucheuma genus or Chondrus genus, and in terms of primary seaweed types, can be sub-classified into kappa-carrageenan, iota-carrageenan and lambda-carrageenan.

In general, in order to form edible aqueous polysaccharides into films, melt-drawing methods cannot be adopted due to restrictions on physical properties, and thus casting methods are generally adopted. For example, filming of pullulan and alginate is carried out by the casting method. However, casting methods wherein water is used as solvent, and the material is formed after drying are employed in order to mold water-soluble polysaccharides, but such methods are currently not used for carrageenan. Specifically, when carrageenan is dissolved in water, cast onto a flat surface and dried, the carrageenan cracks during drying, and it is not possible to obtain the material in the form of a proper film. Moreover, although it is possible to obtain a carrageenan film during drying, the water content in the carrageenan must be high in such cases, and the film will undergo local deformation due to local stress when it is removed, making it difficult to obtain a flat film. In addition, films will be extremely difficult to handle because they will readily stick to each other, so obtaining the material in the form of a wound-up film would be impossible.

The inventors of the present invention et al., as a result of investigations regarding films having carrageenan as a primary component, made the surprising discovery that film forming properties are dramatically improved when galactomannan is added to carrageenan.

The present invention is a water-soluble polysaccharide film, characterized by containing carrageenan and galactomannan in a weight ratio of 99:1 to 20:80.

It is difficult to obtain a good film-form material by casting galactomannan solution on a flat surface and then drying it to remove the water content, because a cracking phenomenon that is similar to that of carrageenan tends to occur. In addition, handling a material with high water content is also difficult due to adhesion between films and the inferior durability of the material in the form of a film. Thus, it is difficult to obtain a good film-form material using casting methods with galactomannan or carrageenan alone.

In contrast, the film of the present invention has dramatically improved film formation properties and almost no cracking, thus allowing the material to be readily

manufactured. In addition, the film of the present invention has the characteristic of high transparency. For example, when carrageenan and locust bean gum, which is a typical galactomannan, are mixed to form an aqueous solution, and the solution is then dried to produce a film, high transparency is obtained that is better than the transparency of films manufactured from carrageenan or locust bean gum alone.

The carrageenan used in the present invention can be kappa, iota or lambda carrageenan, or mixtures thereof. In addition, it is preferable for the carrageenan to be a purified product produced by extraction from the seaweed carrageenan source, followed by filtration, purification and powdering. However, crude product can also be used that has been obtained simply by washing the source seaweed with water, drying, and powdering the material. However, when a film with high transparency is to be produced, it is desirable to use purified carrageenan rather than crude carrageenan.

On the other hand, examples of galactomannan that can be used include guar gum and locust bean gum. When a film with high transparency is to be manufactured, it is preferable to use a material with high purity as the galactomannan. Alternatively, components other than carrageenan and galactomannan such as flavorings or colorants can also be added in levels at which film forming properties are not compromised.

In manufacturing the film of the present invention, the carrageenan and galactomannan are first dissolved in solvent, ordinarily water. When water-soluble polysaccharide is dissolved, inorganic salts or water-soluble organic solvents may be added to the water in order to prevent undissolved clumps from appearing, and in order to improve dispersibility. Examples of inorganic salts that can be used include sodium chloride, potassium chloride, sodium sulfate and potassium sulfate. It is preferable for the amount of inorganic salts used to be 10% or less with respect to the water. Examples of water-soluble organic solvents include methanol, ethanol, propanol and acetone. The added amount of organic solvent is preferably 25% or less with respect to the water.

When producing the solution of carrageenan and galactomannan, after dissolving the two substances separately in solvent, these solutions can then be mixed, or alternatively, the two powders can be dissolved in the same solution. When the solvent is heated and the water-soluble polysaccharides are added, dissolution can be facilitated by stirring.

The ratio of water-soluble polysaccharides in the solution is 1-80 parts by weight of galactomannan relative to 99-20 parts by weight of carrageenan. If the amount of carrageenan is outside this range, cracking will occur during casting, and film manufacture will not be possible. If the amount of galactomannan is outside this range,

on the other hand, cracking will frequently appear during film manufacture, and it will be extremely difficult to manufacture a film.

Next, using a casting method, the film is manufactured by casting the water-soluble polysaccharide solution in a container having a flat surface, and then drying the solution. Film manufacture by means of casting methods can be carried out in batch format or continuous format.

Examples of materials that can be used for the container having a flat surface include glass, stainless steel, Teflon and stone. In order to obtain a film with uniform thickness, it is preferable to use glass or stainless steel. However, Teflon and stone are superior from the standpoint of providing good film peeling properties.

The container is then left alone, and the water content is removed by ambient drying, air drying or other means, thus producing the film of the present invention.

It has been stated that the water content present in a film is generally an important factor in the phenomenon of cracking or film adhesion in water-soluble polysaccharide films. However, the ratio of carrageenan and galactomannan has a greater influence than does water content. For example, when a film is manufactured using a smooth plate made from glass by casting the carrageenan solution on the smooth surface and drying it, if the water content of the carrageenan is less than 20%, then cracking will be extreme during drying, and it will not be possible to form a good film.

If the water content is 20% or greater, on the other hand, the carrageenan coating will have a certain degree of toughness, thus reducing cracking, but the film will still be brittle with respect to strain applied during peeling. As a result, it will be difficult to obtain a good film. If the water content is too high, on the other hand, then the coatings will adhere to each other, and it will be difficult to obtain a wound-up film-form material. Moreover, problems will occur with non-uniformity in thickness and smoothness due to strain applied in separating the film from the flat surface. Specifically, with carrageenan alone, there is essentially no range of water content whereby cracking can be minimized while providing a film with excellent durability.

When using galactomannan without carrageenan, on the other hand, cracking occurs during drying when the water content of the galactomannan is less than 15%, and a good film is not obtained. However, if the water content is 15% or greater, the galactomannan coating will be endowed with a certain degree of toughness, thus reducing cracking, but the film will still be brittle with respect to strain applied during peeling, and so it will be difficult to obtain a good film. If the water content is too high, on the other hand, the coatings will adhere to each other, making it difficult to obtain a wound-up film-form material. Moreover, the galactomannan coating will break due to strain

applied during separation of the material from the smooth surface, thus producing effects whereby good coatings cannot be obtained. Consequently, with galactomannan alone, there is essentially no range of water content whereby good film formation can occur, as when carrageenan is used alone.

In contrast, in the carrageenan and galactomannan mixed system used in the present invention, cracking will not occur over a broad range of water contents of 5-100% when the film is separated from the smooth surface after drying. In addition, it will be possible to readily separate the film from the smooth surface.

The water-soluble polysaccharide film of the present invention can be used as an edible film in applications that include wafers, instant foods, edible printed films, binders for drug products, films for tablet molding and culture media.

The water content in the working examples and comparative examples below was determined by means of drying the films for 4 h at 105°C and measuring the drying weight loss. Transparency was measured at a wavelength of 620 nm using a visible spectrophotometer. The film thickness was measured with a dial gage thickness measurement device. Measurement of the rupture strength was carried out by maintaining a sample strip with a length of 70 mm and a width of 10 mm overnight under conditions of 20°C and 60% RH, and performing tensile testing at a pull rate of 60 mm/min under conditions of 20°C and 60% RH with the testing device set to a chuck separation of 50 mm.

#### Working Example 1

5 g of kappa carrageenan obtained by extraction from Philippine *Eucheuma cottonii*, followed by filtration and drying (water content 9%) were dispersed in 250 mL of deionized water, and was stirred for 3 h at 80°C to obtain a solution.

Meanwhile, crude locust bean gum powder obtained from the Portuguese carob tree was dissolved in hot water, and was subjected to filtration and drying. 5 g of the resulting purified locust bean gum (water content 12%) were dispersed in 250 mL of deionized water, and were dissolved by stirring for 3 h at 80°C. The two aqueous solutions obtained by the processes described above were then mixed, and were stirred for 1 h at 80°C. 300 mL of this solution were then poured, while hot, uniformly onto a rectangular stainless steel plate with a length of 30 cm and a width of 40 cm having a bottom surface that was sufficiently smooth. Subsequently, the material was dried overnight in a vacuum dryer at 70°C. When the plate was removed after drying,

absolutely no cracking was observed. When the film was carefully peeled, it separated readily in a single piece from the stainless steel plate. The water content of the film immediately after removal from the dryer was 8%, and the water content was 18% after having been left indoors for 1 h after peeling.

In addition, an aqueous solution produced by diluting the aforementioned mixed aqueous solution 10x with deionized water was used, and a film with a thickness of 5  $\mu\text{m}$  was obtained. The infrared spectrum of the material is presented in the figure.

#### Comparative Example

10 g of the same carrageenan as used in Working Example 1 (water content 9%) were dispersed in 500 mL of deionized water, and were dissolved by stirring for 3 h at 80°C. 300 mL of this solution were then poured, while hot, uniformly onto a rectangular stainless steel plate with a length of 30 cm and a width of 40 cm having a bottom surface that was sufficiently smooth, and the material was then dried overnight in a vacuum dryer at 70°C. After drying, the plate was removed for observation, and innumerable cracks of indeterminate form were produced in the carrageenan. It was impossible to remove a film having a surface area of 5  $\text{cm}^2$  or greater. The water content immediately after removal of the carrageenan was 12%.

The transparency of the split strips was 89%, and the thickness was 51  $\mu\text{m}$ .

#### Working Example 2

5 g each of the kappa carrageenan and purified locust bean gum used in Working Example 1 were mixed in powder form, and were then infused with 50 mL of methanol. The substances were then dispersed in 500 mL of water, and were dissolved by stirring for 3 h at 80°C. 300 mL of this solution were then poured, while hot, uniformly onto a rectangular stainless steel plate with a length of 30 cm and a width of 40 cm having a bottom surface that was sufficiently smooth, and the material was dried overnight in a vacuum dryer at 70°C. After drying, the plate was removed, but no cracking was observed. A good film was formed. The water content of the film was 10% immediately after removal from the dryer.

### Comparative Example 2

10 g of purified locust bean gum of the same type as used in Working Example 1 (water content 12%) were dispersed in 500 mL of deionized water, and were then dissolved by stirring for 3 h at 80°C. 300 mL of this solution were then poured, while hot, uniformly onto a rectangular stainless steel plate with a length of 30 cm and a width of 40 cm having a bottom surface that was sufficiently smooth, and the material was dried overnight in a vacuum dryer at 70°C. After drying, the plate was removed and observed, and innumerable indeterminate cracks were found in the locust bean gum. A film with a surface area of 5 cm<sup>2</sup> or greater could not be removed.

The water content of the resulting separated strips was 10% immediately after removal.

The transparency of the divided sheets was 85%, and the thickness was 53 µm.

### Working Example 3

3 g of iota carrageenan obtained by extraction from Philippine *Eucheuma spinosum*, followed by filtration and drying (water content 7%), were dispersed in 250 mL of deionized water and dissolved by stirring for 3 h at 80°C. Meanwhile, 5 g of crude locust bean gum powder of the same type as used in Working Example 1 were dispersed in 250 mL of deionized water, and were stirred for 3 h at 80°C to dissolve it. The two aqueous solutions obtained by the above processes were stirred for 1 h at 80°C.

150 mL of this solution were then poured, while hot, uniformly onto a rectangular glass dish with a length of 30 cm and a width of 20 cm having a bottom surface that was sufficiently smooth. Subsequently, the material was dried overnight in a vacuum dryer at 75°C. After drying, the plate was removed. Cracking was not observed when the film was removed from the glass dish, and a good film was produced. The water content immediately after removing the film from the vacuum dryer was 8%.

### Working Example 4

9 g of the same purified carrageenan as used in Working Example 1 and 1 g of the same purified locust bean gum as used in Working Example 1 were mixed as powders, and were then dispersed in 500 mL of deionized water, followed by stirring for 3 h at

80°C to dissolve the substances. 300 mL of this solution were then poured, while hot, uniformly onto a Teflon plate with a length of 30 cm and a width of 40 cm having a bottom surface that was sufficiently smooth, and was then dried overnight in a vacuum dryer at 65°C. After drying, the plate was removed, but no cracking was observed. It was thus possible to peel the material to obtain a good film, and the water content of the film was 13% immediately after removal from the dryer.

#### Working Example 5

The carrageenan was 3 g of commercially-available carrageenan (Genugel LC-4, manufactured by Copenhagen Pectin), and the galactomannan was 5 g of purified guar gum (water content 15%) obtained by overnight dissolution of commercially-available guar gum (*Emko Gum CSAA*, manufactured by Meyhall), followed by filtration and reprecipitation. The substances were mixed in powder form, and dispersed in 500 mL of deionized water. The materials were then stirred for 3 h at 80°C to dissolve them. 300 mL of this solution were then poured, while hot, uniformly onto a Teflon plate with a length of 30 cm and a width of 40 cm having a bottom surface that was sufficiently smooth, and was dried overnight in a vacuum dryer at 70°C. After drying, the plate was removed and observed, but absolutely no cracking was found. In addition, the film readily peeled to produce a good film. The water content of the film was 15% immediately after removal from the dryer.

#### Working Example 6

3 g of commercially-available carrageenan (Newgelin LB-4, manufactured by Chuo-Kasei), and 7 g of unpurified commercially-available locust bean gum (*Emko Gum Fururu M-200*, manufactured by Meyhall) were mixed in powder form, and dispersed in 500 mL of deionized water. The materials were then stirred for 3 h at 80°C to dissolve them. 300 mL of this solution were then poured, while hot, uniformly onto a stainless steel plate with a length of 30 cm and a width of 40 cm having a bottom surface that was sufficiently smooth, and was dried overnight in a vacuum dryer at 60°C. After drying, the plate was removed, but absolutely no cracking was observed. In addition, the film



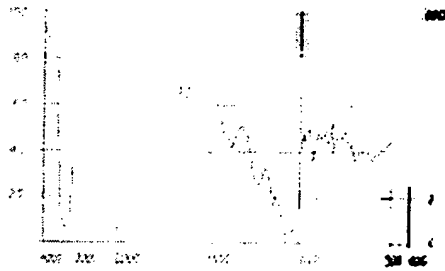
could be readily peeled to produce a good film. The water content of the film was 18% immediately after removal from the dryer.

The thicknesses, transparencies and rupture strengths of the films obtained in Working Examples 1-6 are presented in the table below.

Working-example no.	1	2	3	4	5	6
Film thickness ( $\mu\text{m}$ )	47	51	39	47	43	53
Transparency (%)	98	98	96	98	98	76
Rupture strength ( $\text{kg}/\text{cm}^2$ )	600	700	620	1100	650	570

#### Brief description of the figure

The figure presents the infrared spectrum of a film having a carrageenan/locust bean gum ratio of



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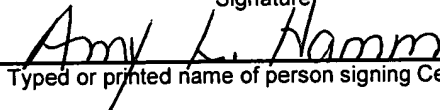
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